BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
A01N 59/16, 59/20, 55/02

A1

(11) International Publication Number: WO 98/58546

(43) International Publication Date: 30 December 1998 (30.12.98)

(21) International Application Number: PCT/US98/12264

(22) International Filing Date: 12 June 1998 (12.06.98)

(30) Priority Data:
08/881,968 25 June 1997 (25.06.97) US

(71)(72) Applicant and Inventor: TAYLOR, John, B. [US/US]; 1420 Lemon Street, Deland, FL 32720–4599 (US).

(74) Agents: HAINES, Warren, M. II et al.; Lathrop & Gage, LC, Suite 2500, 2345 Grand Boulevard, Kansas City, MO 64108 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: FUNGICIDAL AND BACTERICIDAL COMPOSITIONS FOR PLANTS CONTAINING COMPOUNDS IN THE FORM OF HEAVY METAL CHELATES

(57) Abstract

The present invention is fungicidal and bactericidal compositions, and methods of use, which provide improved efficacy in controlling parasitic fungi and bacterial infections in plants. The compositions have fungicidally and bactericidally effective amounts of heavy metal chelates in aqueous solution. Such compositions control fungal and bacterial attacks on plants substantially nonphytotoxic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TITLE

FUNGICIDAL AND BACTERICIDAL COMPOSITIONS FOR PLANTS CONTAINING COMPOUNDS IN THE FORM OF HEAVY METAL CHELATES

INVENTOR(S)

John B. Taylor

1420 Lemon Street

Deland, Florida 32720-4599

FIELD OF THE INVENTION

The present invention is broadly concerned with fungicidal and bactericidal compositions, and methods of use, which provide improved efficacy in controlling parasitic fungi and bacterial infections in plants. More particularly, the compositions and methods of use of the invention including fungicidally and bacterially effective amounts of copper compounds in form of heavy metal chelates, and preferably in the form of Cu-EDDHA, cupric ethylene diamine dio-hydroxyphenylacetate in aqueous solution).

BACKGROUND OF THE INVENTION

Fungicides, as well as bactericides, are chemical agents used to protect agricultural crops from those pathogens which, if left uncontrolled, would result in unacceptable economic losses.

Copper compounds that are active as fungicides and bactericides have been in agricultural use since the advent of Bordeaux in the grape vineyards of France in the early 1800's. Many different formulations of fungicides employing copper compounds, such as wettable powders, water based flowables and dry flowables, are commonly used today in modern agricultural applications.

Such copper compounds, for the most part, have been inorganic in form when applied to agricultural uses. Organic forms of the copper compounds have been found to be generally phytotoxic, especially in foliar applications. (Certain organic copper compounds, however, have some utility as fungicides (e.g., CUTRINE Cu salt of triethanole amine) is quite effective as an aquatic algaecide.)

Modern day agricultural use of inorganic copper compounds as fungicides employ varying forms of copper compounds having relatively low water solubility, including for example, cupric hydroxide, tri basic copper sulfate and tank mix combinations (with heavy metal ethylene bis dithiocarbamate fungicides to enhance the bactericidal activity against certain important agricultural bacteria such as Xanthomonas, Pseudomonas, and Erwinia).

Water soluble copper compounds such as $CuSO_4$, though effective to inhibit germination of fungus spores, cannot be used in foliar applications to agricultural crops because the cupric ion is extremely phytotoxic. Therefore, relatively insoluble forms of inorganic copper compounds, such as cupric hydroxide, have been found to be more effective fungicides. (Not all water insoluble Cu compounds are fungicidal or bactericidal. It is known that the in vitro fungicidal activity is largely dependent on its solubility in the spore exudate and in the fungal cell.)

The problem with popular copper fungicides is that, because they are largely water insoluble, they are normally applied in relatively large volume aqueous suspensions and, as such, are readily removed by rain. Frequent applications are thus necessary at short intervals -- an application process which is expensive and environmentally imprudent.

Therefore, the need exists for a highly water soluble Cu compound based fungicide and bactericide that avoids the problems associated with phytotoxicity experienced in the past with such compounds. A need also exists for such a water soluble Cu compound based fungicide and bactericides that reduces the adverse Cu load on the plant, thus reducing the non target impact to the environment. Further, a need exists for such fungicidal and bactericidal compounds that permits use of other heavy metals such as manganese, zinc, iron, copper and mixtures thereof, as may be desired to for specific fungicidal or bactericidal properties.

SUMMARY OF THE INVENTION

The present invention address the problems outlined above, and provides an improved anti-fungal and anti-bacterial compositions for plants that contains, as active ingredients, fungicidally and bactericidally effective amounts of heavy metal chelates in aqueous solution. According to the present invention, it has been discovered that the application to the plant of the inventive composition substantially eliminates fungus and bacteria disease, while at the same time, is substantially non-phytotoxic.

Thus, an object of the present invention is to provide a fungicidal composition for protection of plants against a fungal infection.

Another object of the invention is to provide such an antifungal protection with a single product that upon application is not excessively phytotoxic.

Another object of the invention is to provide a method for treating plants and to provide anti-fungal protection for plants against attack by fungus. Yet, further

object of the invention is to provide an anti-fungal composition for treating plants that is environmentally safe, inexpensive to use and has low mammalian toxicity.

Thus, an object of the present invention is to provide a bactericide composition for protection of plants against a bacterial infection.

Another object of the invention is to provide a composition employing heavy metal chelates that functions as both a fungicide and bactericide.

These and other objects of the invention are obtained by invention disclosed below.

According to one aspect of the invention, anti-fungal compositions for the protection of plants preferably contain, as an active material, a fungicidally effective amount of a heavy metal chelate in mixture with an agriculturally acceptable carrier such as water. According to another aspect of the invention, anti-bacterial compositions for the protection of plants preferably contain, as an active material, a bactericidally effective amount of a heavy metal chelate in mixture with an agriculturally acceptable carrier, such as water.

According to another aspect of the invention, a single composition having both fungicidal and bactericidal qualities is provided and contains fungicidally and bactericidally effective amounts of heavy metal chelates in mixture with an agriculturally acceptable carrier such as water.

The fungicidal and bactericidal compositions each preferably employ a heavy metal chelate selected from the group consisting of Fe-EDDHA (ethylene-diamine di (O-hydroxy phenylacetate)), Cu-EDDHA, Mn-EDDHA, and Zn-EDDHA and mixtures thereof.

According to another aspect of the invention, the amount of heavy metal chelate is from about 0.01 to about 1.0 pounds AI per acre.

A DESCRIPTION OF THE DRAWINGS:

Fig 1 is the chemical structure for Fe EDTA (iron chelate of ethylene diamine tetraacetic acid).

Fig 2 is the chemical structure for FE DTPA (iron chelate of diethylene-triamine pentaacetic acid).

Fig 3 is the chemical structure for Fe EDDHA (iron chelate of ethylene dihydroxyphenylacetic acid) or as listed in the U.S. Patent 2,921,847 ferrous and ferric-APCA (iron chelates of ethylene bis(alpha imino-ortho-hydroxyphenylacetic Acid)).

Fig 4 is the chemical structure for Fe pEDDHA (iron chelate of para ethylene diamine dihydroxyphenylacetic acid).

Fig 5 is the chemical structure for Fe EDDHMA (iron chelate of ethylene diamine dihydroxyphenylmethylacetic acid).

Fig 6 is the chemical structure for Cu EDDHA (copper chelate of ethylene diamine dihydroxyphenylacetic acid).

A DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The following examples set forth preferred concentrations and techniques for formulation thereof, as well as methods of application and use in test results, demonstrating the efficacy of the inventive concentration in protecting plants against attack by fungi or bacteria, or both. It is to be understood, however, that these Examples are presented by way of illustration only and nothing therein shall be

taken as a limitation upon the overall scope of the invention. The specific components tested in the Examples were prepared and applied as follows:

Cu-EDDHA was and can be prepared using the process disclosed in U.S. Patent 2,921,847, the teachings of which are hereby incorporated herein by reference. The '847 patent describes the process for the preparation of Fe-EDDHA, which in the '847 patent is referred to as ferrous and ferric-APCA (iron chelates of ethylene bis(alpha amino-ortho-hydroxyphenylacetic acid). To prepare Cu-EDDHA, an appropriate Cu salt need merely be substituted for the iron salts disclosed in the '847 patent. Likewise, other heavy metal chelates disclosed herein may be prepared by substituting the desired heavy metal for Cu in the process disclosed in the '847 patent. The chemical structure for Cu-EDDHA is illistrated in Fig. 6. The chemical structures for other common heavy metal chelates are illistrated in the following figures: Fig. 1 Fe-EDTA; Fig. 2, Fe-DTPA; Fig. 3, Fe-EDDHA; Fig. 4, Fe-pEDDHA; and Fig 5, Fe-EDDHMA.

METHOD OF APPLICATION

The preferable method of application is foliar, either by ground or aerial equipment, but is not limited to that method alone. Injection or soil applications, for example, can also be applications depending upon specific crops and pathogens.

The inventive compositions have utility on fruit crops, and agronomic crops, ornamentals, trees, grasses, vegetables, grains, and flori cultural crops, as well as, some aquatic crops including rice.

The fungicidal and bactericidal properties of the compounds according to the invention are various, but are particularly interesting in the case described in the following examples:

As used in the Examples, "Ave. % infection" means percent of leaves that exhibit fungus lesions.

EXAMPLE 1

Cu-EDDHA and four commercially accepted fungicidal compositions were applied to Valencia orange on sour orange rootstock. Applications were in 100 gallons of solution (in the concentrations indicated) per acre in mid-summer to single-tree plots replicated six times in a randomized complete block ("RCB") design. Seven months later the percentages of citrus greasy spot infection on five branch terminals from each tree were recorded and averaged.

CITRUS GREASY SPOT TEST

CAUKINS GROVES, INDIANTOWN, FLORIDA

	TREATMENT	RATE/100 GAL.	* AVE % INFECTION 2/10/88
1)	FCC-455 Spray Oil (Fla. Citrus Commission)	1%	30.0
2)	Difenconazole	50 g ai	1.56
3)	Difenconazole	100 g ai	1.0
4)	Cu-EDDHA 3.2%	0.2 lb ai	2.5
5)	KOCIDE 101	4 lbs.	23
6)	Untreated	—	35

APPL. Single tree plots x 6 Reps.

* Aug. 5 terminals/tree

Difenconazole: 1-[2-[4-(4-chlorophenoxy)-2-chlorophenyl-(4-methyl-1, 3-dioxolan-2-yl)-methyl]]-1H-1,2,4-triazole (available from Ciba-Geigy, Greenbough, N.C.)

Cu-EDDHA: sodium cupric ethylene-diamine di (o-hydroxyphenylacetate).

KOCIDE 101 available from Griffin Corp., Valdosta, Ga.

* % infection of citrus greasy spot (Mycosphaerella citri)

EXAMPLE 2 FUNGICIDE

Cu-EDDHA, TILT (propiconzaole-Ciba-Geigy) and difenconozole were applied in 100 gpa to single tree plots of "Valencia" oranges replicated five times in a RCB design in mid-July.

Twenty mature leaves (from the spring flush) per replicate were harvested approximately 4 months later and placed under greenhouse conditions and alternately wetted and dried to simulate natural defoliation and weathering.

These conditions in turn cause the fungus to sporulate by the formation of perithecia (spore production body of fungus) which were counted as a means of measuring the fungicidal activity of the treatments. These data are presented below.

CITRUS GREASY SPOT

SCN NURSERY, DUNDEE, FLORIDA

	TREATMENT	RATE/100 GAL.	#PERITHECIA
1)	Cu-EDDHA 3.2%	0.2 lb ai	3.24 b
2)	Cu-EDDHA 3.2%	0.4 lb ai	5.93 ab
3)	TILT 3.6 EC	6 oz. Prod.	6.62 ab
4)	Difenconzaole	100 g ai	5.32 ab
5)	Difenconazole	200 g ai	11.57 ab
6)	CONTROL inoculated		7.97 ab
7)	CONTROL not inoculated		6.42 ab

Function: ANOVA—1

Date case no. 1 to 42

Without selection

One way ANOVA grouped over variable 1

TREATMENT NUMBER

with values from 1 to 7

Variable 3

NUMBER OF PERITHECIA PER 5MM FIELD AT 2.5 X —MEAN OF THREE OBSERVATIONS

ANALYSIS OF VARIANCE TABLE

	Degrees of Freedom	Sum of Squares	Error Mean Square	F-value	Prob.
Between	6	226.6508	37.78	1.33	.270
Within	34	965.0170	28.38		
Total	40	1191.6678			

EXAMPLE 3 FUNGICIDE

Cu-EDDHA, Kocide (cupric hydroxide) and difenconazole were applied to single tree plots of "Hamlin" oranges in 100 gpa (in concentration indicated) in a RCB design replicated 4 times. Applications were made in May, June and May and June. Ten fruit/replicate were sampled in July and percent infection of Melanose (Diaporthe citri) was determined. See data presented below.

CITRUS MELANOSE CONTROL

R.E. KEENE FRUIT COMPANY

TREATMENT	RATE LBAI/100 GAL.	TIMING	% INFECTION (FRUIT)
Cu-EDDHA 3.2%	0.2	May	9
Cu-EDDHA 3.2%	0.4	May	13
Cu-EDDHA 3.2%	0.8	May	21
Cu-EDDHA 3.2%	0.2	May-June	11
Cu-EDDHA 3.2%	0.4	May-June	15
Cu-EDDHA 3.2%	0.8	May-June	29
Cu-EDDHA 3.2%	0.2	June	14
KOCIDE	4.0	May	12
KOCIDE	0.4	May-June	10
DIFENCONAZOLE	0.5	June	4
Untreated	—	—	38

4 REPS SINGLE TREE PLOTS.

PENETRATOR (surfactant - non-ionic)@ 4 oz. ALL TREATMENTS

EXAMPLE 4 FUNGICIDE

GRAPEFRUIT (Citrus paradisi 'Marsh')

Greasy spot; Mycosphaerella citri

GREASY SPOT CONTROL ON LEAVES, 1986-87: Spray treatments were applied dilute (applied to point of run off) by handgun in July to 10-ft-high trees at a rate equivalent to 700 gal/acre. Treatments were replicated on 8 single-tree plots in a RCB design. Groups of 15 shoots on each of the east/west and east side of each tree were tagged and the initial number of leaves was recorded. In February, remaining leaves were counted and examined for greasy spot.

All treatments except Difolatan (fungicide) reduced greasy spot-induced defoliation and the percentage number of remaining leaves with greasy spot symptoms. There were no significant differences in effectiveness between Tribasic copper sulfate, spray oil, Spotless, Tilt, and Cu-EDDHA. There was too little greasy spot rind blotch in this test to provide information on the relative efficacy of treatments for preventing fruit infection.

Treatment and rate/100 gal	defoliation	% remaining leaves with greasy spot
Tribasic copper sulfate (53% Cu) 0.75 lb	1.9 a	20.1 a
Sunspray 7E oil 1 gal	3.1 a	27.0 a
Difolatan 80 Sprills 1.25 lb	8.9 b	49.8 b
Spotless 25W 0.8 lb	1.3 a	22.6 a
Tilt 3.6EC 8 fl oz.	1.5 a	15.9 a
Cu-EDDHA (3.2% Cu) 1.5 gal	0.8 a	12.0 a
Untreated	9.7 b	48.5 b

EXAMPLE 5 FUNGICIDE

Cu-EDDHA, TILT (propinconazole), difenconozole and MERTECT (Merck Chem., N.J.) (thiabendazole) were applied in 100 gpa to 2-year-old laurel oaks (Quercus hemispherica) in 2x2 gal. pots in a RCB design replicated 4 times. Applications were made in July approximately 3 weeks apart and rated in August a month later. See data below.

OAK LEAF BLISTER (Taphrina caerulescens) CONTROL

TRAILRIDGE NURSERY, KEYSTONE HEIGHTS, FLORIDA

TREATMENT	RATE/PROD 100 GAL.	*DISEASE INDEX
1) Tilt 3.6 emulsifiable	8 oz	1.5
2) Difenconazole 3.6 emulsifiable	2 oz	2.25
3) Cu-EDDHA 3.2	8 oz	2.8
4) MERTECT	8 oz	1.5
5) Untreated	—	4.25

* Disease Index: Rated 8/26/86.

1 = no disease
2 = light
3 = moderate
4 = heavy
5 = dead foliage

2 x 2 gal trees/exp. unit x 4 Reps in a RCB design

EXAMPLE 6 BACTERICIDE

Cu-EDDHA and Kocide (cupric hydroxide) were applied as foliar spray in May to Hibiscus sinensis cuttings (100/replicate) x 4 replicates in a RCB design. Treatments were allowed to dry for one hour and then placed in a commercial propagation bed under intermittent mist and rated for bacterial (Erwinia chrysanthemi) infection one week later. Data presented below.

*ERWINIA CONTROL ON HIBISCUS

NELSONS NURSERY, APOPKA, FLORIDA

TREATMENT	RATE/CU 100 GAL.	AVG. % INFECTION
1) Cu-EDDHA 3.2%	0.2 lb. ai	6
2) Cu-EDDHA 3.2%	0.4 lb. ai	8
3) KOCIDE 101	2 lbs. ai	25
4) Untreated	—	100

100 Cuttings/REP X 4 *ERWINIA chrysanthemi

EXAMPLE 7 BACTERICIDE

A follow-up experiment to EXAMPLE 6 was conducted on rooted cuttings which were dipped as they were removed from the propagation bed and foliarly sprayed 7 days later after being potted. Cu-EDDHA and Kocide were applied at the rates specified below in a RCB design utilizing 100 plants/replicate x 4 reps. Potted cuttings had not received any previous bactericide treatments prior to potting.

ERWINIA CONTROL ON HIBISCUS

NELSONS NURSERY—APOPKA, FLORIDA

TREATMENT	RATE/LBAI 100 GAL.	AVE. % INFECTION
Cu-EDDHA 3.2%	0.2	19
Cu-EDDHA 3.2%	0.8	32
KOCIDE	2.0	22

APPLIC. DATES: 7/19 DIP, 7/26/85 SPRAY

100 PLANTS/REP. X 4

EXAMPLE 8 BACTERICIDE

Control of Bacterial Spot on Pepper Plants

With Stage II Bactericides

Procedure—Early Cal Wonder variety pepper plants were treated at weekly intervals with the following bactericides (g ai/liter): copper + mancozeb (2 + 1), Cu-EDDHA (0.1), CGA (Ciba-Giegy of America -- Bactericides)-115944, CGA-151731, CGA-157566, and CGA-164058 (each at 0.25 and 0.5), CGA-143268 (1.0). Treatments were applied weekly in 1000 l/ha for a total of eight applications. The crop was artificially inoculated after the first and third applications. Disease severity was evaluated after the fourth and eight applications. Phytotoxicity was rated after the eight application and yields were taken continually during the test.

Results—Disease pressure was moderate and uniform. After four applications, the best treatments were CGA-115944, CGA-151731, and CGA-164058. CGA-157566 was less effective than the three previously mentioned compounds but more effective than CGA-143268 which was equal to copper plus mancozeb and Cu-EDDHA in activity. The ranking of compounds changed when treatments were rated 12 days after the last application. Copper plus mancozeb control has completely broken down, which was expected because disease conditions were severe in the final half of the test and copper should be applied on a five-day schedule under these conditions. Cu-EDDHA at only 0.05X the rate of Kocide 101 (on a metallic copper basis) was exhibiting some control and was equal to CGA-143268, CGA-157566, and CGA-164058. The best bactericide at the second rating were CGA-115944 and CGA-151731. The phytotoxicity of all treatments was assessed after eight applications had been made. The only bactericides which were phytotoxic were CGA-115944 and CGA-164058. CGA-164058 was safer than

CGA115944 which was marginally unacceptable at 0.5 g ai/1. CGA-143268 and CGA-164058 increased yields dramatically. Yields were depressed by CGA-0115944, CGA-151731, and CGA-157566. Cu-EDDHA had no effect on yield and copper + mancozeb increased yields moderately. In summary, several compounds showed excellent activity, but none had sufficient crop safety.

EXAMPLE 9 BACTERICIDE

Cu-EDDHA at 0.2 and 0.4 lbs. ai/100 gal. and Kocide 101 at 7.4 lbs. ai/A were applied as foliar applications to croton (Codiaeum variegatum) previously inoculated with Xanthomonas campestris a day earlier. Treatments were assigned in a RCB design and replicated 10 times with single pots. Treatments were applied 3 times on a weekly schedule and evaluated at 7 and 14 days following the last application. See data below.

Test 1 Codiaeum Inoculated with Xanthomonas

Number of leaves with symptoms

TREATMENT	RATE/100 GAL. a.i.	AVE. % INFECTION
Water	noninoculated	0 a
Water	inoculated	2.6 c
Cu-EDDHA 3.2%	26 ml (.2 lb.)	.6 ab
Cu-EDDHA 3.2%	52 ml (.4 lb.)	1.0 b
Kocide 101	6.8 ml. (7.4 lb.)	.9 ab

ANOVA table

Source	Sum of squares	df	Mean square	F Value
Treatment	37.28	4	9.319	9.177
			significant at 1% level	
Error	45.7	45	1.016	
Total	82.98	49		

All of the copper treatments provided some control of Xanthomonas leaf spot of Codiaeum, when compared to the inoculated control. The lower rate of Cu-EDDHA and the Kocide 101 gave control equal to the noninoculated control treatment.

CARROT/ALTERNARIA FUNGICIDE TRIAL

		AVG % INFECTION	
TREATMENT	**RATE/100 GAL.**	**04/05/96**	**04/23/96**
1) K-PHOS	1%	6.9	8.2
2) PHOS-MIGHT	1%	18.7	28.8
3) K-PHOS + PHOS-MIGHT	0.5% + 0.5%	8.9	10.7
4) Cu-EDDHA	0.2 lb ai	8.8	11.6
5) Fe-EDDHA	0.2 lb ai	12.7	12.9
6) Untreated	—	23.0	34.8

*EDDHA (ethylene-diamine di (O-hydroxy phenylacetate)

PLOT SIZE: Single Row X 25 ft. X 4 reps in a RCB design.

Application dates: 2/2, 9,15,22,3/8,14,22, and 28. Rated 4/5 and 4/23/96

NOTE: Second rating was 25 days after last fungicide application. Plots were inoculated with Alternaria dauci

Sanford, FL

K-PHOS (Commercially available and is sold under trademark "K-Phos" by Foliar Nutrients, Inc., Cairo, GA 31724) (K_2HPO_4, 0-18-20)

PHOS MIGHT (Commercially available and is sold under trademark "Phos Might" by Foliar Nutrients, Inc., Cairo, GA 31724) (K_2HPO_3, 0-22-20)

EXAMPLE 15 - FUNGICIDE

CRAPE MYRTLE POWDERY MILDEW CONTROL

TREATMENT	RATE/100GAL.	AVG % INFECTION FL GL	FOLIAGE
1) K-PHOS	1%	12.0	22.50
2) Cu-EDDHA	0.2 lb ai	11.20	16.4
3) Fe-EDDHA	0.2 lb ai	6.4	0
4) K-PHOS	1%	4.2	0
+			
Cu-EDDHA	0.2 lb ai	100	100

FL.GL. = unopended flower clusters (2/trtm X 4 reps)

Foliage (2 terminals - 10 leaves X 4 reps in RCB design).

Crape Myrtle (Lagerstromia indica)

Powdery Mildrew (Erysiphe lagerstroemiae)

App. dates: 5/23, 30th and 6/6. Rated: 6/9

K-PHOS - (K_2HPO_4, 0-18-20) ("K-Phos" is a trademark of Foliar Nutrients, Inc., Cairo, Ga.)

The above Examples demonstrate that the inventive compositions are useful in protecting plants against attack by fungus with the application of the inventive solution.

It will be further appreciated that foliar application of the inventive compositions will be effective as a common agricultural practice to control bacterial infections in plants.

As used herein, the term "heavy metal chelate" is intended to refer to an organic coordination "complexing" compound in which a metal ion is bound to atoms of non-metals, e.g., nitrogen, carbon or oxygen, to form a hetrocylic ring having coordinate covalent bounds. The non-metal atoms may be attached to the metal ions by from one to six linkages and, thus, are called uni-, bi-, tri- dentate, etc., meaning 1-, 2-, or 3-tooth. Heavy metals, such as cobalt, copper, iron, nickel, zinc, magnesium and platinum are metal ions that are commonly involved in chelate structures. Examples of heavy metal chelate structures include:

Fe-HEEDTA (hydroxy ethylenediamine triacetic acid), Fe-EDTA (ethylenediamine tetra acetic acid), Fe-DTPA (diethylene triaminepenta acetic acid), Fe-EDDHA (ethylene dihydroxyphenylacetic acid), ethylene bis dithiocarbamates of Mn- and Zn-, Cu-EDDHA, Mn- and Zn-EDDHA.

As used herein, unacceptably high levels of phytotoxicity is intended to mean foliar burn, defoliation and stem die-back, or necrosis, plant stunting or death. Phytotoxicity is also rated on an international scale of 0-10 where 0 is equal to no phytotoxicity and 10 is complete death of the plant.

Heavy metal chelates disclosed herein are possess water solubility acceptable for use in the inventive fungicide and bactericide.

For example, the solubility of sequestrene 138 Fe Iron Chelate in pounds per 100 gallons of water, at various temperatures (solubility weight/100 gals. H_2O) is shown in Table 1 below:

Temperature (°C)	Lbs.
0	69
10	70
20	75
30	81
40	84
50	88

Commercially produced Sequestrene 138 Fe contains 6% Iron as metallic, or 8.5% iron as Fe_2O_3. The commercial product has a moisture content of not more than 10%.

Without being limited to this theory, it is believed that heavy metal chelation generally increases water solubility of the heavy metal ion and the availability in certain soil conditions of the metal ion where calcareous and high pH situations would otherwise prevent metal ions from being available to the plant as a fungicide.

It is believed that certain heavy chelates (usually in the form of Mn, Zn, and Fe) may be applied foriarly at much reduced rates when compared to inorganic salts intended for fungicidal and bactericidal use.

Ranking of Fe chelates used in foliar applications are as follows: Fe-HEEDTA -- most phytotoxic; Fe-EDTA -- intermediate phytotoxic, Fe-DTPA -- less phytotoxic, and Fe-EDDHA -- least phytotoxic. Such rankings do not necessarily apply when the chelate is EBDC fungicides in the Mn, Zn form.

It will be appreciated by those skilled in the art that beneficial effects demonstrated in the Examples by the use of Cu-EDDHA will also be obtained when

the Mn, Zn and Fe forms EDDHA and other forms of heavy metal chelates are employed.

CLAIMS

What is claimed is:

1. A fungicidal composition for controlling fungus disease in plants comprising:

a fungicidally effective amount of a heavy metal chelate in aqueous solution.

2. The composition according to Claim 1, wherein the heavy metal is selected from the group consisting of manganese, zinc, iron, and copper, and mixture thereof.

3. The composition according to Claim 1, wherein the amount of said heavy metal chelate is present in aqueous solution from about 0.01 to about 1.0 pounds AI per acre.

4. A method of controlling fungus disease in plants comprising:

applying to the plant in fungicidally effective amounts a heavy metal chelate in aqueous solution.

5. A method according to Claim 4, wherein said solution comprises an aqueous solution, wherein said heavy metal chelate is present in solution from about 0.01 to about 1.0 pounds AI per acre.

6. A bacterial composition for controlling bacteria disease in plants comprising:

a bacterially effective amount of a heavy metal chelate in aqueous solution.

7. The composition according to Claim 6, wherein the heavy metal is selected from the group consisting of manganese, zinc, iron, and copper.

8. The composition according to Claim 6, wherein the amount of said heavy metal chelate is present in aqueous solution from about 0.01 to about 1.0 pounds AI per acre.

9. A method of controlling bacteria disease in plants comprising:

applying to the plant in bacterially effective amounts a heavy metal chelate in aqueous solution.

10. A method according to Claim 9, wherein said solution comprises an aqueous solution, wherein said heavy metal chelate is present in solution from about 0.01 to about 1.0 pounds AI per acre.

11. A fungicidal and bactericidal composition for controlling fungus and bacteria disease in plants comprising:

a fungicidally and bactericidally effective amount of a heavy metal chelate in aqueous solution.

12. The composition according to Claim 11, wherein the heavy metal is selected from the group consisting of manganese, zinc, iron, and copper, and mixture thereof.

13. The composition according to Claim 11, wherein the amount of said heavy metal chelate is present in aqueous solution from about 0.01 to about 1.0 pounds AI per acre.

14. A method of controlling fungus and bacterial disease in plants comprising:

applying to the plant in fungicidally and bactericidally effective amounts a heavy metal chelate in aqueous solution.

15. A method according to Claim 14, wherein said solution comprises an aqueous solution, wherein said heavy metal chelate is present in solution from about 0.01 to about 1.0 pounds AI per acre.

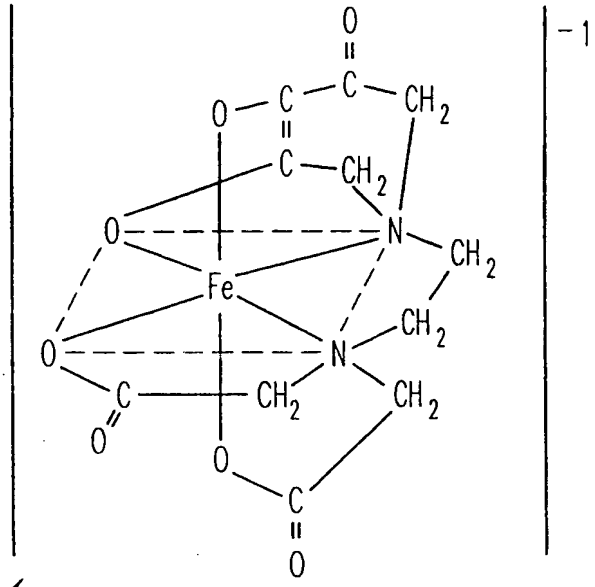
O
C
C
CH2
O
C
CH2
O
N
CH2
Fe
CH2
O
N
C
CH2
CH2
O
O
C
O
C
O
-1

Fig. 1

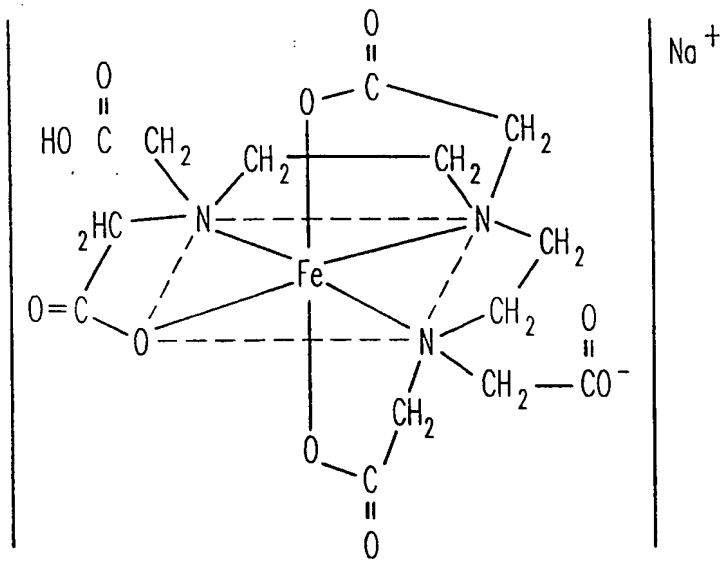
O
C
O
CH2
HO
C
CH2
CH2
CH2
2HC
N
N
CH2
Fe
O=C
O
CH2
O
N
CH2
CO-
CH2
O
C
O
Na+

Fig. 2

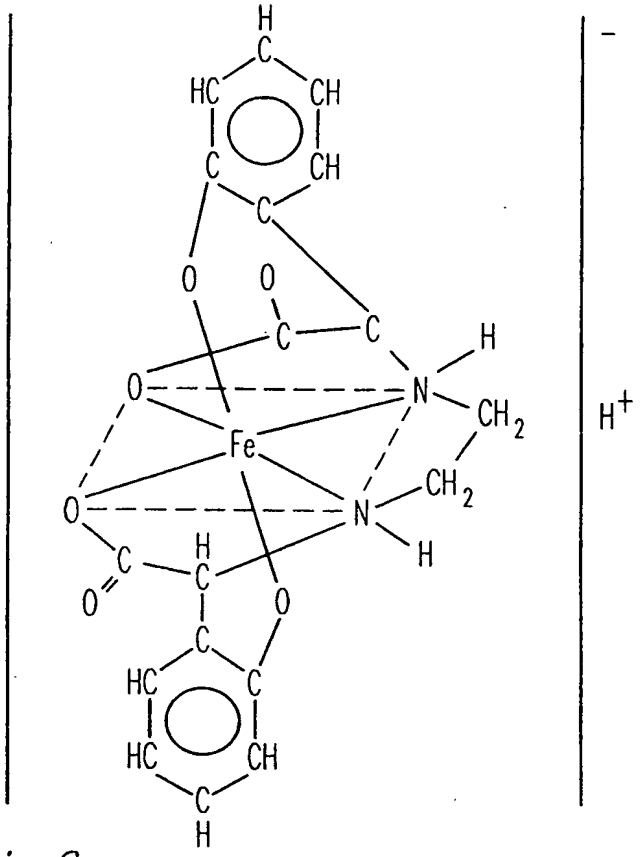

Fig. 3

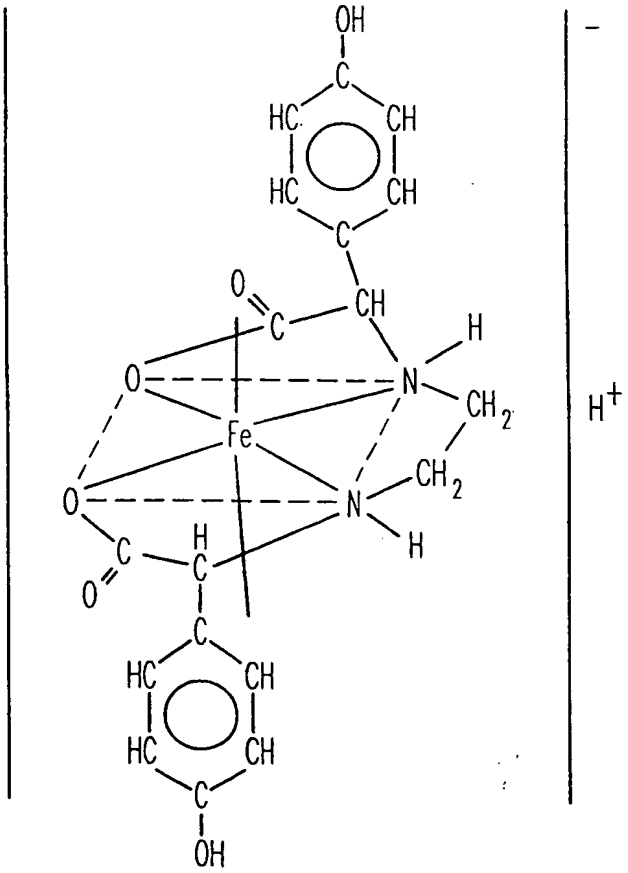

Fig. 4

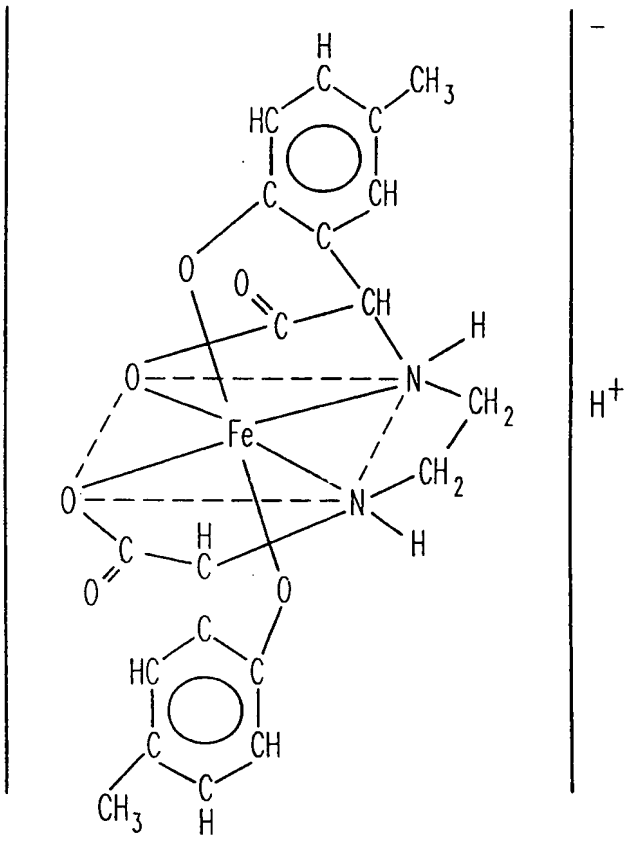
H
C
CH3
HC
C
CH
C
C
O
O
C
CH
H
O
N
CH2
Fe
CH2
O
N
H
C
H
C
O
O
C
HC
C
C
CH
C
CH3
H
H+
−

Fig. 5

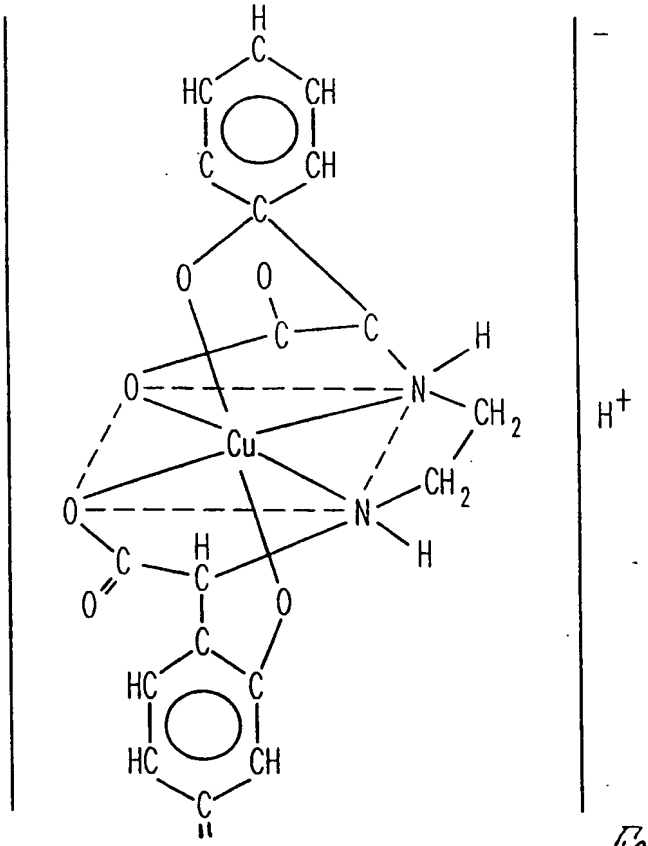
H
C
HC
CH
C
CH
C
O
O
C
C
H
O
N
CH2
Cu
CH2
O
N
H
C
H
C
O
O
C
HC
C
HC
CH
C
H+
−

Fig. 6

INTERNATIONAL SEARCH REPORT

In ational Application No
PCT/US 98/12264

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N59/16 A01N59/20 A01N55/02

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 401 059 A (ROQUETTE FRÈRES) 5 December 1990 * the whole document*	1-15
X	US 2 921 847 A (KNELL ET AL.) 19 January 1960 cited in the application * the whole document*	1-15
X	DATABASE CABA PEER ET AL. : "Control of fusarium wilt in carnation grown on rockwool by pseudominas sp. strain WCS417r and by Fe-EDDHA" XP002079868 AN 91:9008 see abstract & NETHERLANDS JOURNAL OF PLANT PATHOLOGY, vol. 96, no. 3, 1990, pages 119-132,	1-5,9-15

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 October 1998	16/10/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Fort, M

2

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/12264

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CABA SKRZYPCZAK ET AL.: "Effect of some fertilizers chelates on the growth of pathogenic fungi and development of disease symptoms on host plants. II: Influence of calcium, iron and zinc on development of Phytophthora foot-rot of Gerbera and population dynamics of Phytophthora cryptogea " XP002079869 AN 97:49819 see abstract & PHYTOPATHOLOGICA POLONICA, vol. 11, 1996, pages 41-50, ---	1-5,9-15
X	DATABASE CABA SKRZYPCZAK ET AL.: "Effect of some fertilizers chelates on the growth of pathogenic fungi and development of disease symptoms on host plants. III. Aster and tulip nutrition with calcium, iron and zinc in relation to disease development and population densities of F. oxysporum f. sp. callistephi and tulipae" XP002079870 AN 97:49820 see abstract & PHYTOPATHOLOGICA POLONICA, vol. 11, 1996, pages 31-40, ---	1-5,9-15
A	DE 35 24 629 A (KUKALENKO) 15 January 1987 see page 3, line 33 - page 5, line 67 ---	1-15
A	US 3 494 945 A (LEWIS ET AL.) 10 February 1970 * the whole document* -----	1-15

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Ir ational Application No
PCT/US 98/12264

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0401059 A	05-12-1990	FR 2647304 A	30-11-1990
		AT 108055 T	15-07-1994
		AU 631850 B	10-12-1992
		AU 5220990 A	29-11-1990
		CN 1047607 A	12-12-1990
		DD 299035 A	26-03-1992
		DE 69010403 D	11-08-1994
		DE 69010403 T	15-12-1994
		DK 401059 T	01-08-1994
		ES 2056398 T	01-10-1994
		HU 209046 B	28-03-1994
		JP 3135904 A	10-06-1991
		PT 93580 A	08-01-1991
		US 5116825 A	26-05-1992
US 2921847 A	19-01-1960	NONE	
DE 3524629 A	15-01-1987	CH 664562 A	15-03-1988
		FR 2583753 A	26-12-1986
		JP 61291591 A	22-12-1986
US 3494945 A	10-02-1970	NONE	